Prediction of transport properties of dense molecular fluids using the effective diameter hard sphere theory

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Prediction of transport properties of dense molecular fluids using the effective diameter hard sphere theory

Perturbation method

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The present paper explores the ability of the effective diameter hard sphere theory to estimate the transport properties of a fluid made up of particles interacting through the Gaussian overlap model. This method relies on the assumption that at high densities the behaviour of a fluid is dominated by harsh repulsive forces. Hence, the properties of the fluid can be given in terms of a hard convex body fluid, and the properties of this fluid can also be expressed in terms of an effective hard sphere fluid. The state-dependent diameter of the reference hard sphere fluid is obtained through the blip function theory, well known in the equilibrium liquid theory of molecular fluids, in terms of the Gaussian overlap model parameters. Comparisons with measured thermal conductivities and shear viscosities for nitrogen and benzene were made, because of the lack of molecular dynamics data. Our results are in good agreement with experimental data over wide density ranges, and the sources of discrepancy could be explained by the fact that the Gaussian overlap model parameters used for those fluids are not accurately determined. Despite this, our results are surprisingly close to experimental determinations.

1. Introduction

Predictions of transport properties (TPs) of molecular fluids in terms of rigorous realistic physical models are difficult to obtain, and further progress is needed. Since the pioneering work of Curtiss and coworkers [1–3], who found a generalized Boltzmann equation for dilute gases in order to include contributions to free streaming and collisions, several routes have been devised mainly for hard convex body (HCB) fluids. These routes follow quite different lines: (1) derivation of kinetic equations for the phase space density [4, 5], with solutions obtained through the Grad's moment method; (2) the use of time correlation functions in conjunction with the method of Ernst to transform the time correlation functions into distribution functions [6]; (3) the use of a Mori-generalized Langevin equation method [7]; and (4) the use of first-order perturbation theory, through the expansion of all terms in the time correlation functions including the propagator [8, 9]. In spite of these formal results, an explicit evaluation of these methods has not been reported.

An alternative route that can deal with realistic intermolecular potentials (making our estimations less dependent on measurements, even when neither the model potential nor the theory is exact) can be developed. This paper therefore addresses the study of transport properties of fluids made up of non-spherical and non-polar molecules, in the dense regime, based on an extension of effective diameter hard sphere theory (EDHST) [10].

The selection of a model potential to mimic the interaction between the particles of our system is the starting point. Although there are several different options, the model must have two basic characteristics: it must be mathematically simple, and it must not violate too strongly our sense of what is physically correct. The potential models mainly considered in the literature for modelling these fluids are: the generalized Stockmayer [11], the Kihara types [11, 12], the site–site types [11], and the Gaussian overlap (GO) [13–21]. For this study we have selected the last model. In the GO model, a molecule is regarded as an ellipsoidal Gaussian distribution of matter density, and it is assumed that when the distributions overlap slightly, the pair potential is proportional to the overlap volume integral of the distributions. The original model was devised primarily to give a simple expression for the orientation dependence of molecular interactions, and further modified to give a realistic r dependence [13]. This model is valid for oblate as well as for prolate shapes of arbitrary anisotropy, and the shape of the molecular core is modelled correctly, at least qualitatively. The main problem with the GO potential is related to the failure to yield correctly some long-range interactions, and of course the correct multipolar behaviour. Some of the most important features of the GO, and its relation with other models, have been reported [14, 16–19]. The GO potential can be expressed as

$$\Phi(\boldsymbol{u}_1, \boldsymbol{u}_2, r) = 4\varepsilon(\boldsymbol{u}_1, \boldsymbol{u}_2) \left[(\sigma(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}})/r)^{12} - (\sigma(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}})/r)^{6} \right], \qquad (1a)$$

with

$$\sigma(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}) = \sigma_0 \left(1 - \frac{1}{2}\chi \left\{ \frac{(\hat{\boldsymbol{r}} \cdot \boldsymbol{u}_1 + \hat{\boldsymbol{r}} \cdot \boldsymbol{u}_2)^2}{1 + \chi \boldsymbol{u}_1 \cdot \boldsymbol{u}_2} + \frac{(\hat{\boldsymbol{r}} \cdot \boldsymbol{u}_1 - \hat{\boldsymbol{r}} \cdot \boldsymbol{u}_2)^2}{1 - \chi \boldsymbol{u}_1 \cdot \boldsymbol{u}_2} \right\} \right)^{-1/2} \qquad (1b)$$

and

$$\varepsilon(\boldsymbol{u}_1, \boldsymbol{u}_2) = \varepsilon_0 \left[1 - \chi^2 (\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)^2 \right]^{-1/2}. \qquad (1c)$$

Here, $\hat{\boldsymbol{r}}$ is the unit vector in the r direction, $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ are unit vectors along the principal axes of the molecules. ε_0, σ_0 and χ are strength, range and anisotropy parameters, respectively. σ_0 and χ can be written in terms of the range parameters $\sigma_\parallel$ and $\sigma_\perp$ characterizing each ellipsoid as

$$\sigma_0 = \sqrt{2}\sigma_\perp, \text{ and } \chi = [\sigma_\parallel^2 - \sigma_\perp^2]/[\sigma_\parallel^2 + \sigma_\perp^2] = [\kappa^2 - 1]/[\kappa^2 + 1]. \qquad (2)$$

Here, κ is the length to breadth ratio of the spheroidal molecules such that $\kappa > 1$ for prolate, and $\kappa < 1$ for oblate molecules.

As mentioned, the shape of the anisotropic molecular core is modelled reasonably well, this is not the case for long-range interactions. This point will be of no consequence in our approach to the transport properties of dense non-spherical fluids, since it seems that the repulsive forces [11], i.e. the shape of the molecules, determine the liquid structure and intermolecular correlations in the same way as in atomic fluids.

In addition, for the anisotropies studied here, we will show that TPs of the GO model fluid can be estimated with a more simple version of this model, i.e. the Gaussian overlap model with constant ε (GOCE) [17].

Once the potential has been selected, our next step would be to use kinetic theory for particles interacting through a potential given by equation (1). However, this is not possible at the present state of the theory. Simpler cases than those related to the HCB mentioned above [4–7] can be used as examples. Efforts to deal with realistic potentials have been reported only for 'simple fluids', i.e. the atomic fluids, and have proved to be difficult [22–25, 31]. Formally, kinetic theory has been developed only for the hard

sphere fluid [26, 27], for the square-well fluid [28–30], and for systems interacting through a spherical hard-core plus an attractive tail [22–25, 27, 31]. Even in these cases, there are several issues still unresolved [25, 30].

Here, we will test a procedure that is an extension of the EDHST [10]. Probably since the time of Enskog, and later with the recognition that the dynamics of liquids are mainly determined by the repulsive part of the interaction potential, there is a common belief that hard sphere expressions can give good estimates of the TPs of actual fluids, if some state-dependent effective hard sphere diameter is used. But, only with the development of kinetic mean field equations could this issue be included in the framework of kinetic theory. There are two lines of approach that give the appropriate theoretical support to the EDHST. The first is based on the maximization of entropy principle subject to constraints developed by Stell and colleagues [22–25, 29]. The second was developed by Sung and Dahler using a Mori–Zwanzig formalism [31]. Sung and Dahler presented the conditions for which the formulas of the Enskog-like theory can be adapted to estimate TPs of fluids modelled with a Lennard-Jones (LJ) potential. These two approaches, derived originally by different means, can be related [25].

To extend EDHST to the case of interest in this paper we make two assumptions. First, the particles in the fluid can be modelled through the GO model. Second, in the dense regime, the dynamics of the fluid are determined mainly by the repulsive part of the non-spherical interaction potential. Hence, following the same line of reasoning as in blip function theory [36–38], the properties of the repulsive system can be given in terms of an appropriate HCB fluid. Thus, a reasonably good representation of the TPs of the GO model fluid at high densities can be obtained through the HCB fluid. However, the TPs of HCB fluids are not known in the dense regime. In a further level of approximation, we can obtain these properties through hard sphere expressions following the procedure given in blip function theory for dealing with non-spherical potentials [38]. Accurate estimates may be expected if the anisotropy of the original molecules to be modelled is not too large. These assumptions have been tested for equilibrium properties of molecular fluids, but they have never been used for transport properties [11, 16, 18, 19, 21].

2. Theory

As mentioned above, the basic idea of our approach is simple, and is responsible for much of the progress achieved in the equilibrium theory of dense molecular liquids. In a dense fluid, the repulsive forces, which are nearly convex hard core interactions, dominate the liquid structure. Hence, we expect that attractive forces, dipole–dipole interactions, and any other slowly varying forces play a minor role in dense fluid behaviour. Thus, if a dense liquid is composed of nearly spherical molecules, the intermolecular structure should be very similar to that of a HCB fluid. This HCB fluid can be described in terms of a fluid made up of hard spheres of an appropriate effective diameter, a fluid that can be handled with hard sphere kinetic theory in order to predict the thermal conductivity (λ) and the shear viscosity (η) of our original fluid, viz., the GO model fluid. Of course, the effective diameter of the hard sphere fluid must depend on the thermodynamic state, to reflect the somewhat soft repulsive r-dependence of the model potential, and on the anisotropy parameters of the GO model. This procedure can be generalized for mixtures, although some additional problems must be solved, as will be presented shortly.

2.1. *Effective diameters*

To obtain the effective diameter for the non-spherical fluid studied here, we use perturbation theory. This approach relates properties of a system, in which the intermolecular pair potential energy is $U(r_{12}, \omega_1, \omega_2)$, with those of a reference system interacting with a potential energy $U_0(r_{12}, \omega_1, \omega_2)$. Here, r_{12} is the vector separating the centres of molecules 1 and 2, with molecular orientations ω_1 and ω_2 ($\omega_i = \phi_i, \vartheta_i, \chi_i$ for nonlinear, and ϑ_i, ϕ_i for linear molecules, respectively). This procedure was developed by several workers using different specific methods [37–41, 16, 21], all inspired by the successful work of Weeks, Chandler, and Andersen (WCA) [36] on atomic fluids. Here, we follow Mo and Gubbins [38]. These authors divided the potential $U(r_{12}, \omega_1, \omega_2)$ into repulsive and attractive regions for each set of molecular orientations. The repulsive part was handled by two consecutive expansions. This splitting of the potential has been studied by molecular dynamics [19], and it takes into account properly the free energy contributions of dense molecular fluids at medium and high densities.

The reference system is made up of rigid HCBs, and the whole theory can be developed in order to give the free energy of this system in terms of a hard sphere system plus additional corrections. Hence, following Mo and Gubbins [38], the Helmholtz free energy of our model potential can be given in terms of the free energy of a system of HCBs interacting through U_0

$$
\begin{aligned}
U_0(r_{12}, \omega_1, \omega_2) &= 0 \qquad r_{12} > d(\omega_1, \omega_2) \\
&= \infty \qquad r_{12} < d(\omega_1, \omega_2)
\end{aligned}
\tag{3}
$$

where $d(\omega_1, \omega_2)$ is the closest (contact) distance of approach of the two molecular centres for fixed orientations ω_1 and ω_2.

The expression of the free energy of the GO model fluid in terms of the hard sphere fluid, and the hard sphere diameter can be obtained as follows. First, our model potential is split into two parts. One involves the repulsive forces, $U_{\rm rep}(r_{12}, \omega_1, \omega_2)$, and the other involves the attractive forces $U_{\rm a}(r_{12}, \omega_1, \omega_2)$. Thus, a potential $V(r_{12}, \omega_1, \omega_2, \alpha)$ is introduced such that

$$
V(r_{12}, \omega_1, \omega_2, \alpha) = U_{\rm rep}(r_{12}, \omega_1, \omega_2) + \alpha U_{\rm a}(r_{12}, \omega_1, \omega_2),
\tag{4}
$$

where

$$
\begin{aligned}
U_{\rm rep}(r_{12}, \omega_1, \omega_2) &= U(r_{12}, \omega_1, \omega_2) + \varepsilon(\omega_1, \omega_2) \quad r_{12} < r_{\min}(\omega_1, \omega_2) \\
&= 0 \qquad\qquad\qquad\qquad\qquad\quad r_{12} > r_{\min}(\omega_1, \omega_2)
\end{aligned}
\tag{5}
$$

$$
\begin{aligned}
U_{\rm a}(r_{12}, \omega_1, \omega_2) &= -\varepsilon(\omega_1, \omega_2) \qquad\qquad\quad r_{12} < r_{\min}(\omega_1, \omega_2) \\
&= U(r_{12}, \omega_1, \omega_2) \qquad\quad r_{12} > r_{\min}(\omega_1, \omega_2).
\end{aligned}
\tag{6}
$$

Here, $\varepsilon(\omega_1, \omega_2)$ and $r_{\min}(\omega_1, \omega_2)$ are the magnitude of $U(r_{\min}, \omega_1, \omega_2)$, and the separation distance, respectively, both evaluated at the minimum of the pair potential (for fixed ω_1, ω_2). Functional differentiation shows that

$$
A_{\rm GO} = A_{\rm rep} + \text{correcting terms.}
\tag{7}
$$

For details see [38]. In a second expansion, $A_{\rm rep}$ is related to the free energy of a system interacting through equation (3), giving

$$
A_{\rm rep} = A_0 + \text{first order terms.}
\tag{8}
$$

The contact distance $d(\omega_1, \omega_2)$ is chosen in such a way to nullify the first-order term

in the free energy expansion, equation (8), in the same way as in the WCA method [36, 41]. Thus, the first-order free energy term vanishes if $d(\omega_1, \omega_2)$ is chosen to satisfy

$$\int_0^\infty dr_{12} r_{12}^2 [1 - \exp(-\beta U_{\text{rep}}(r_{12}, \omega_1, \omega_2))] Y_0(r_{12}, \omega_1, \omega_2)$$

$$= \int_0^{d(\omega_1, \omega_2)} dr_{12} r_{12}^2 Y_0(r_{12}, \omega_1, \omega_2). \tag{9}$$

Since the fluid interacting through the potential given by equation (3) is unknown, it is necessary to go to the second level of approximation. Using Bellemans' [43] method, which should apply provided the anisotropy is not too great, the contact distance $d(\omega_1, \omega_2)$ can be expanded as

$$d(\omega_1, \omega_2, \alpha) = d_0 + \alpha \gamma(\omega_1, \omega_2) d_0, \tag{10}$$

where $\gamma(\omega_1, \omega_2)$ is defined so that $d(\omega_1, \omega_2, \alpha = 1) = d(\omega_1, \omega_2)$, and d_0 is the effective hard sphere diameter given by

$$d_0 = \langle d(\omega_1, \omega_2) \rangle_{\omega_1, \omega_2}. \tag{11}$$

From here, it is possible to obtain working equations for the free energy in terms of a hard sphere fluid of diameter d_0 plus a few corrections. Mo and Gubbins [38] extended the work of Verlet and Weis [41] for atomic fluids, and gave an analytical expression for $d(\omega_1, \omega_2)$ in the form

$$d(\omega_1, \omega_2) = d_{\text{B}}(\omega_1, \omega_2) \left[1 + \frac{\sigma_1(\omega_1, \omega_2)}{2\sigma_0(\omega_1, \omega_2)} \delta(\omega_1, \omega_2) \right], \tag{12}$$

where d_{B} is the Barker–Henderson contact distance

$$d_{\text{B}}(\omega_1, \omega_2) = \int_0^\infty dr_{12} [1 - \exp\{-\beta U_{\text{rep}}(r_{12}, \omega_1, \omega_2)\}], \tag{13}$$

and

$$\delta(\omega_1, \omega_2) \cong \int_0^\infty dr_{12} \left[\frac{r_{12}}{d_{\text{B}}(\omega_1, \omega_2)} - 1 \right]^2 \frac{\partial}{\partial r_{12}} \exp[-\beta U_{\text{rep}}(r_{12}, \omega_1, \omega_2)]. \tag{14}$$

The approximate expressions for $\sigma_0(\omega_1, \omega_2)$ and $\sigma_1(\omega_1, \omega_2)$ are

$$\sigma_0(\omega_1, \omega_2) = \frac{(2 - \eta)}{2(1 - \eta)^3} \tag{15a}$$

$$\sigma_1(\omega_1, \omega_2) = \sigma_0(\omega_1, \omega_2) + \frac{(1 - 5\eta_w - 5\eta_w^2)}{(1 - \eta_w)^3} - \frac{27\eta_w^3 (1 - 0 \cdot 717\eta_w - 0 \cdot 114\eta_w^2)^2}{2(1 - \eta_w)^6 (1 - \eta_w/2)}, \tag{15b}$$

where

$$\eta = \frac{\pi}{6} \rho [\langle d(\omega_1, \omega_2) \rangle_{\omega_1, \omega_2}]^3 \tag{15c}$$

$$\eta_w = \eta - \eta^2/16 \tag{15d}$$

hence, the hard sphere diameter d_0 can be obtained from the closed set of equations (10–15).

There is another way to obtain an effective diameter for non-spherical molecules. This method uses a variational technique. Here, the Gibbs–Bogoliubov inequality is used to obtain an upper bound for the Helmholtz free enrgy of the system. This is a direct extension of the work of Rasaiah and Stell [49] dealing with upper bounds for free energies of atomic fluids in terms of a hard sphere fluid. We will present our results using this procedure in a forthcoming paper.

2.2. *Explicit formulas for the transport properties*

As mentioned, for the case of the LJ system there are two well connected starting points in order to obtain a procedure giving good estimates of TPs, based on kinetic mean field theories [22, 31]. But, for the interaction potential of interest here, there are no fundamental works that establish rigorously the conditions for which the formulas of Enskog theory could be applicable. Thus, an adaptation of the Enskog theory for fluids interacting through the GO model is implemented here, following the same line of reasoning presented in the previous section for obtaining the thermodynamic properties, and with the procedure of Sung and Dahler [31] given for the LJ interaction as a guide.

Following our basic assumptions, the TPs of our model system in the dense regime can be estimated through the evaluation of the TPs of the hard sphere fluid with effective diameter d_0. We hope that this procedure will improve the estimation of TPs of actual fluids, since there is a large body of evidence [32–35] that supports the idea that the predictions of the Enskog theory can be made to agree with the experiment quite well, when an effective diameter is introduced. The actual potential in these fluids is probably better modelled with a three-parameter potential like the GO model.

The hard sphere kinetic theory that will be used here, is the so called revised Enskog theory (RET) first derived by van Beijeren and Ernst [26]. Here, the hard sphere radial distribution function is the same function of the number density as the radial distribution function of a system in non-uniform equilibrium. The RET equation can be solved by the use of the Chapman–Enskog method. The molecular fluxes and the transport coefficients for a dense hard sphere fluid, up to the Navier–Stokes level, can be obtained directly on the basis of the procedure used in [27] and [44]. Here, we present only the final expressions to obtain the TPs for pure fluids:

$$\eta = \frac{1}{\chi^c}\left[1 + \frac{4}{5}\left(\frac{2}{3}\pi n\sigma^3\chi^c\right) + 0.7615\left(\frac{2}{3}\pi n\sigma^3\chi^c\right)^2\right]\eta_0 \qquad (16)$$

$$\lambda = \frac{1}{\chi^c}\left[1 + \frac{6}{5}\left(\frac{2}{3}\pi n\sigma^3\chi^c\right) + 0.7575\left(\frac{2}{3}\pi n\sigma^3\chi^c\right)^2\right]\lambda_0, \qquad (17)$$

where

$$\eta_0 = \frac{5}{16\pi\sigma^2}(\pi m k T)^{1/2} \qquad (18)$$

$$\lambda_0 = \frac{75k}{64\pi\sigma^2}\left(\frac{\pi k T}{m}\right)^{1/2}. \qquad (19)$$

Here, n is the number density, σ the hard sphere diameter, m the mass of the particle, χ^c the pair distribution at contact, T the absolute temperature, and k Boltzmann's constant.

The evaluation of equations (16) and (17) requires knowledge of χ^c. We used the

Table 1. Parameters.

| | Nitrogen | | | | Benzene | |
	GOCE[a]	LJ1[b]	LJ[c]	GOCE1[a]	GOCE2[a]	LJ1[b]
$\sigma_0/\text{Å}$	3·37	3·798	3·6502496	6·3	6·474	5·349
$(\varepsilon_0/k)\text{K}^{-1}$	94	71·4	100·01654	300	265	412·3
κ	1·3	1	1	0·5	0·5	1

[a] GOCE from [14].
[b] Lennard-Jones from [61].
[c] Lennard-Jones from [52].

approximate expression of Carnahan and Starling [45], since it appears to be quite accurate when compared with molecular dynamics (MD) data.

MD calculations have proved that Enskog's expressions for transport coefficients are not exact, since these do not take into account velocity correlations in the dense regime. Correction multiplicative factors to the Enskog expressions have been given by Dymond [46] (Dymond's correction) for shear viscosity and thermal conductivity although, for the case of shear viscosity, van der Gulik and Trappeniers [47] have modified these expressions on the basis of the computations given by Michels and Trappeniers [48]. The correction factors are

$$
\begin{aligned}
C_\eta &= 1\cdot02 + 10\cdot61(n^* - 0\cdot495)^3 + 247\cdot49\,(n^* - 0\cdot813)^3 \quad n^* > 0\cdot813 \\
&= 1\cdot02 + 10\cdot61(n^* - 0\cdot495)^3 \qquad\qquad\qquad 0\cdot593 < n^* < 0\cdot813 \\
&= 1\cdot02 \qquad\qquad\qquad\qquad\qquad\qquad\qquad 0\cdot593 > n^* \qquad (20a)
\end{aligned}
$$

$$
C_\lambda = 0\cdot99 + 0\cdot1597\,n^* - 0\cdot7464\,n^{*2} + 1\cdot2115\,n^{*3} - 0\cdot5583\,n^{*4}. \quad (20b)
$$

In all the above equations $n^* = n\sigma^3$.

3. The sources of experimental data

To make a stringent test of the predictive capability of EDHST for predicting transport properties of the GO model fluid, experimental data from MD simulations are needed. But, as far as we know, there are no MD data for transport properties involving the GO model. Although some MD data have been reported for molecular fluids [50, 51], they are not useful in the discussion of our results. Hence, we used experimental data to make our comparisons, although only very few fluids have been characterized in the context of the GO model. We obtained from the literature [14] the GO model parameters (ε_0, σ_0 and κ) for nitrogen, benzene, and carbon dioxide.

It is clear that this comparison could not be a good test of our procedure, not only by the fact that actual fluids do not interact through the GO model, but also since there is not enough information to support the quality of the reported parameters in the estimation of transport properties. TPs appear to be quite sensitive to the potential parameters, at least this is the case for atomic fluids. As a matter of fact, for our case the parameters were determined in order to fit thermodynamic properties [14].

For comparison with experimental data for nitrogen and benzene we used the parameters given in table 1 for our model potentials. There are one set of GOCE parameters for nitrogen, and two sets for benzene. In addition, this table includes several sets of parameters for the usual LJ potential for those systems. They will be used in our comparisons later. Carbon dioxide was not studied here, since the GO parameters reported in [14] do not fit the experimental data therein.
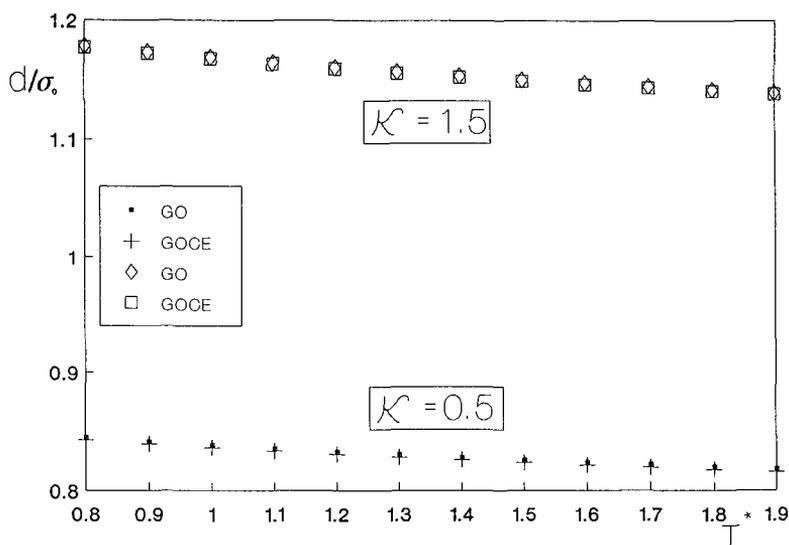
Figure 1.   Effective diameters as a function of the reduced temperature $T^* = kT/\varepsilon_0$, for GO and GOCE model potentials at two length to breadth ratios ($\rho\sigma_0^3 = 0\cdot6$).

Accurate experimental data for nitrogen were obtained from [52] and [54], and for benzene [53] and [55].

4.   Results and discussion

With the above procedure, our first step was to evaluate the effective hard sphere diameters in different thermodynamic states. In figures 1 and 2, some examples of calculated effective diameters are shown for different anisotropy parameters. In these
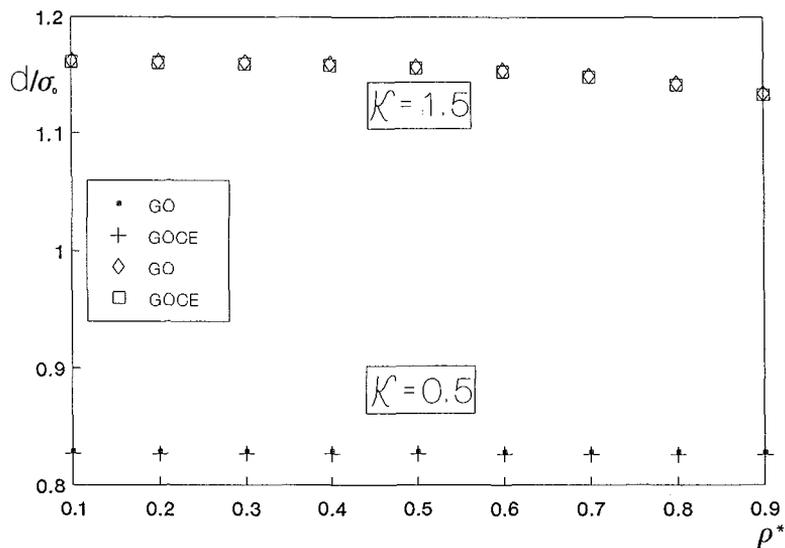

Figure 2.   Effective diameter as a function of the reduced density $\rho^* = \rho\sigma_0^3$, for GO and GOCE model potentials at two length to breadth ratios ($kT/\varepsilon_0 = 1\cdot4$).
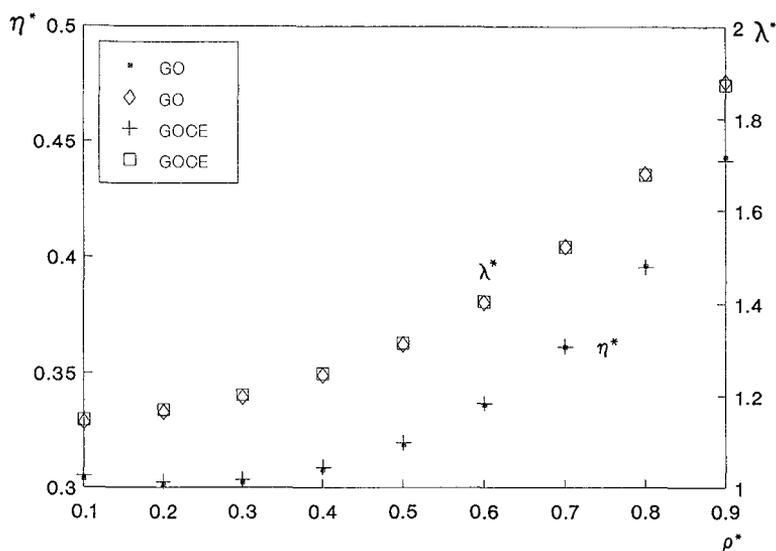
Figure 3.   Transport properties ($\eta^* = \eta\sigma_0^2/\sqrt{m\varepsilon_0}$, $\lambda^* = \lambda\sigma_0^2/k\sqrt{m/\varepsilon_0}$) given by EDHST as a function of the reduced density $\rho^* = \rho\sigma_0^3$, evaluated for systems interacting with GO and GOCE model potentials ($\kappa = 0.5$, and $kT/\varepsilon_0 = 1.4$).

figures, we can see that these effective diameters, as expected, decrease as the temperature increases, and for densities above $\rho^* = 0.5$ they decrease as density increases. As mentioned in the introduction, since the strength parameter ε is a weak function of molecular orientation for the anisotropic molecules studied here, we have therefore neglected the variation in well depth. Thus, we have used ε as a constant obtaining the GOCE model where $\varepsilon = \varepsilon_0$. This enables us to make our calculations simpler, and it does not have any adverse consequences in the thermodynamics and the transport properties. From figures 1 and 2, note that, in the same thermodynamic state, GO and GOCE give essentially the same effective diameter. The difference is negligible, and it does not have any influence in the final calculations of transport properties, as can be seen in figure 3 for $\kappa = 0.5$.

Figure 4 shows our predictions for the shear viscosities of liquid N_2, modelled with the GOCE model potential, along the coexistence curve. In addition, figure 4 shows the experimental data, and calculations for the shear viscosity of N_2 modelled with LJ. The calculations for LJ were done following the same theory as presented here, but for the spherical case [10, 22]. That is, given an LJ potential and using the corrected version of the WCA method presented by Verlet and Weis [42], an effective diameter depending on the thermodynamic state can be obtained. With this diameter and equations [16–20], transport properties for the LJ system can be given. For details see reference [10]. It is important to mention that for the case of LJ, with EDHST, it is possible to obtain predictions closer to the experimental data if the effective diameters are obtained with a variational technique [10].

In figure 4, the predictions of our theory are shown to be good, taking into account that the GOCE parameters given in [14] were not obtained from a rigorous study for fitting transport data, as is the case for the LJ parameters. It is clear that a greater error can be introduced by the different sets of LJ parameters currently used in the literature.
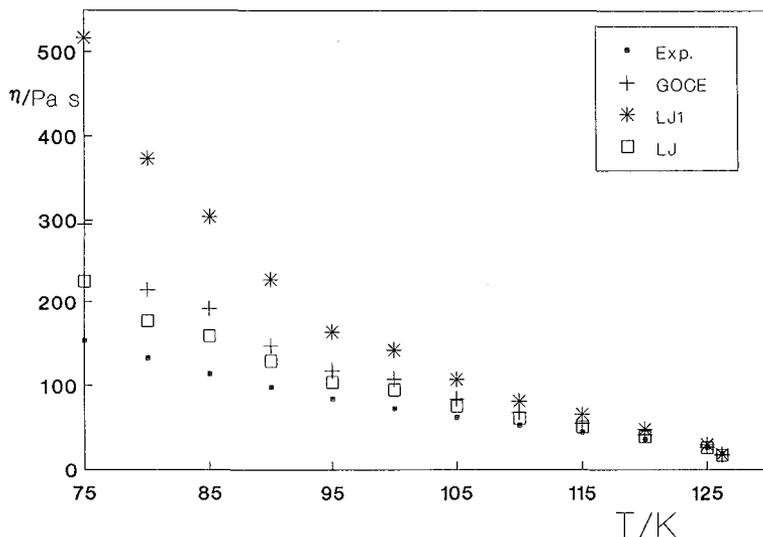
Figure 4.   Comparison between shear viscosity calculations for N_2 along the liquid coexistence curve, and experimental data. Calculations were performed with EDHST for N_2 modelled with GOCE potential, and with LJ potential (parameters given in table 1).

Figure 5 presents our calculations for the shear viscosities of fluid N_2 as a function of the density at constant temperature, together with experimental data, and calculations for nitrogen modelled with the GOCE model and with the LJ. Here, in a broad density range, the EDHST for the GOCE model behaves correctly $(\rho \leq 0\cdot6)$, although it overestimates at high densities. This overestimation increases a little with temperature. In figures 4 and 5, at high densities, the LJ gives the best fit, probably due to the better quality of the parameters used.
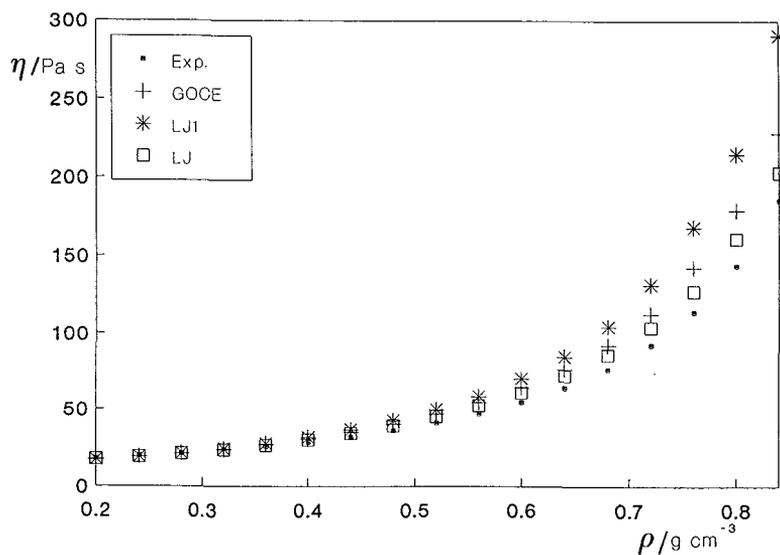

Figure 5.   Comparison between shear viscosity calculations of fluid N_2 modelled with GOCE potential and with LJ potential, and experimental data, at $T = 250\,K$.

An important point is that in our approach the rotational degrees of freedom are ignored. For thermal conductivity a contribution of rotational and other internal degrees of freedom is expected, although in the range of few per cent [32]. To improve the EDHST results some corrections due to the internal degrees contribution can be introduced. In this paper we follow a heuristic approach followed by some authors [56, 57, 60] and suggested by previous work by Mason and Monchick [58] on the basis of the Wang Chang–Uhlenbeck–De Boer theory [59], to deal with polyatomic gases in the dilute regime. Mason and Monchick showed that λ can be separated effectively into two parts: one dealing with the transfer of thermal energy due to the translational motion of the molecules, and one dealing with the transfer of energy due to changes in the internal energy of the molecules. Here, we assume that λ of a dense fluid can be split into a part due to the energy transfer by molecular motion and collisional transfer (λ'), given by EDHST, and a part due to the energy transfer associated with the internal degrees of freedom of the molecules through diffusion (λ''). Terms involving the interchange of translational and internal energy through inelastic collisions have not been considered. This correction will improve the EDHST results mainly at moderate densities. Thus,

$$\lambda = \lambda' + \lambda''. \tag{21}$$

In addition, we assume that λ'' can be represented by the first order approximation formula given by Mason and Monchick for quasielastic collisions:

$$\lambda'' = \rho D C_v''/M = \lambda_0''/\chi^c \tag{22}$$

where D is the self-diffusion coefficient, and λ_0'' is the internal contribution to λ for the dilute hard sphere gas, C_v'' is the molar heat capacity at constant volume for the internal degrees of freedom, and M is the molecular weight.

To obtain a general formula for the evaluation of λ_0'', for real fluids, the modified Eucken correlation for polyatomic gases was used [60, 62],

$$\lambda_0'' = \frac{f_{\text{int}} \left(C_p^\circ - \frac{5}{2} R \right) \eta_0}{M} \tag{23}$$

where η_0 is the dilute gas viscosity, C_p° is the ideal gas molar heat capacity, R is the gas constant, M is the molecular weight, and f_{int} has a constant value of 1·32.

C_p° values for different systems were obtained through a temperature expansion up to the sixth order: we used the expansions that appear in the TRAPP computer program developed by Ely and Hanley [60].

Figure 6 presents our calculations for the thermal conductivity of liquid N_2 along the coexistence line, and figure 7 shows the density dependence of thermal conductivity in the fluid phase, also for N_2, at constant temperature. As above, we included in these figures the experimental data and the predictions for GOCE model and for the LJ potential. We included for all these cases the correction for λ'' as given in equations (22) and (23). Also in these figures we show the calculations for GOCE, but without including this correction due to the internal degrees of freedom. Figure 6 shows, in general, very good agreement. The predictions for the GOCE model give better results than for any LJ. The contribution of the internal degrees clearly corrects the calculations mainly in the less dense region, as expected, but at very high densities, there is a little overestimation.

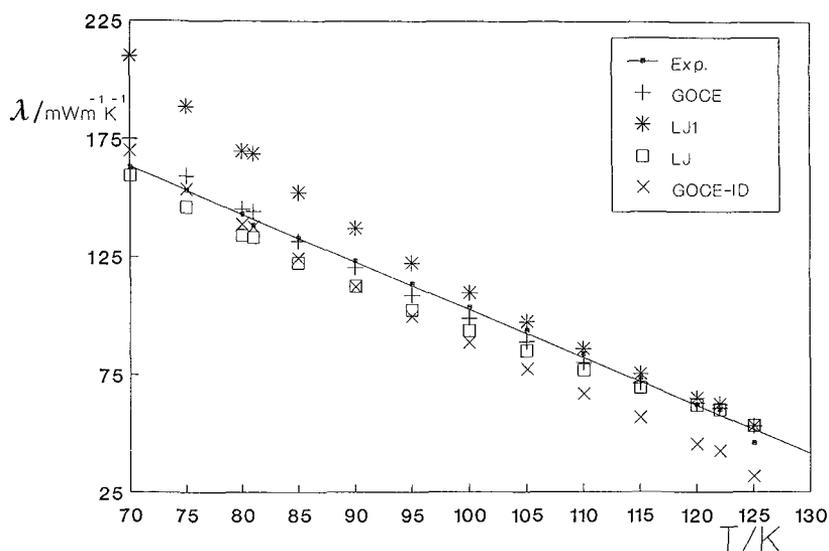In figure 7, we can see how the contribution due to the internal degrees changes

Figure 6.   Comparison between thermal conductivity calculations for N_2 along the liquid coexistence curve, and experimental data. Calculations were performed with EDHST. N_2 was modelled with GOCE potential (GOCE) and with LJ potential (LJ and LJ1). The parameters are given in table 1. In these cases, we included a correction due to the contribution of internal degrees. GOCE-ID denotes calculations with EDHST for N_2 with GOCE, but without the correction due to the contribution of internal degrees. The solid line is drawn through the data points as a guide to the eye.
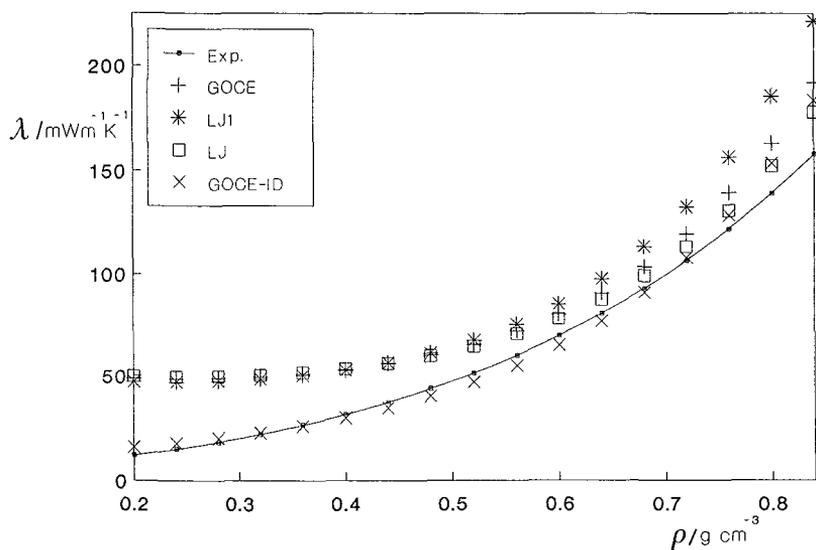

Figure 7.   Comparison between thermal conductivity calculations of N_2 modelled with GOCE potential and with LJ potential, and experimental data, at $T = 130$ K. Notation as for figure 6.
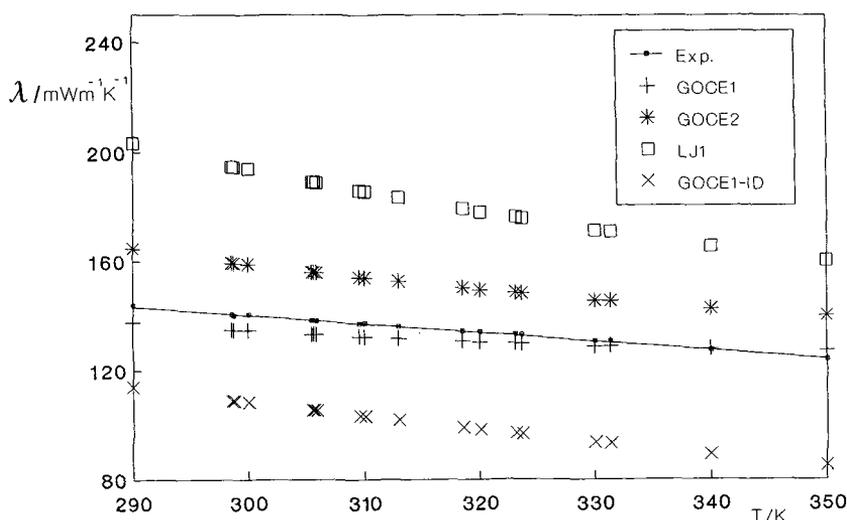
Figure 8. Comparison between thermal conductivity calculations for benzene along the liquid coexistence curve, and experimental data. Calculations were performed with EDHST. Benzene was modelled with GOCE potential (GOCE1 and GOCE2) and with LJ potential (LJ). The parameters are given in table 1. In these cases, we included a correction due to the contribution of internal degrees. GOCE1-ID denotes calculations with EDHST for benzene with GOCE, but without the correction due to the contribution of internal degrees. The solid line is drawn through the data points as a guide to the eye.

the good fitting of the predictions for GOCE not including this contribution. This is more noticeable at moderate and low density regions. It is difficult at this point to determine the exact origin of this problem. One possibility could be that formulas (22) and (23) are unable to give the proper contribution due to internal degrees of freedom. But, the more acceptable possibility is related to the procedure used to obtain the effective diameter. There is clear evidence [32, 10] that the thermal conductivity is somewhat overestimated in this region ($\rho \leq 0.4$) when the procedure described in this paper is used for the case of the LJ, due to the breakdown of the WCA assumptions. We consider that the failure of our calculations to fit the thermal conductivity at medium and low densities for N_2 using the GOCE model is due to the same problem.

Figure 8 presents our calculations for the thermal conductivity of liquid benzene along the coexistence curve. As before, we presented in this figure the experimental data, and our calculations for benzene modelled with the GOCE model and with the LJ potential. The correction due to internal degrees was included in these cases. We also included here our calculations for GOCE without the contribution of internal degrees. For this figure, we used two sets of GOCE parameters as given in [14]. The parameters labelled as GOCE1 gave the best fit to the experimental data. Here, it is clear that our approach to the estimate of TPs using GOCE1 or GOCE2 gives better results than using any LJ.

Also we can see from figure 8 that our approach is sensitive to the selection of GOCE parameters. This is due to the high sensitivity of the hard sphere expressions for the TPs to variations in the hard sphere diameter. Thus, small variations in the GOCE parameters produce, through the effective diameter, quite different TPs. In this way, slightly different fluids can give significant different TPs. The behaviour of the TPs as a function of the parameters of the model potential, i.e. the geometry of the

molecules, is not easy to see. For a given number density and temperature, the TPs are functions of the effective diameter $d_0 = d_0(\varepsilon_0, \sigma_0, \kappa)$ and, depending on how the parameters defining the model potential are arranged, they will influence the TPs.

As expected, test calculations of transport properties for carbon dioxide gave bad results. This confirms that the GOCE parameters given in [14] must be improved.

In summary, the procedure presented in this paper constitutes the first attempt to predict numbers for transport properties of molecular fluids. The results are encouraging, since some examples have given very good results. The conclusions drawn from our calculations are not clear enough in all cases. Although this procedure is conceptually more elaborate than those using the LJ, MD data for transport properties of GO fluids are needed to determine if our procedure is a good option to give accurate estimates of TPs for non-spherical fluids. We hope this type of study will motivate work in this direction. The approach can be improved in several ways: one is the use of other schemes to obtain the effective diameter. The variational method has given very good results when fluids are modelled with the LJ potential [10]. This study is underway and will be published shortly. Another area that deserves more careful study is the contribution of internal degrees to thermal conductivity. The procedure used here, although very common, must be refined with more powerful theories [63].

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